

# Photoacoustic Methane Detection using a novel DFB-type Diode Laser at 3.3 $\mu\text{m}$

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## Abstract:

To the best of our knowledge, we present for the first time spectroscopic methane measurements with a DFB-type laser diode at a wavelength of approximately 3.3  $\mu\text{m}$ . The laser diode can be operated near room temperature and emits a maximum of 1.5 mW optical power with a spectral line width smaller than 10 MHz. This novel kind of semiconductor laser allowed performing precise photoacoustic measurements of characteristic methane absorption structures in the  $\nu_3$  band. In addition, the setup enables high detection sensitivity with a limit in the ppb range.

**Key words:** DFB-type laser diode, photoacoustic measurements, methane, isotopologues, ppb-range

## Introduction

The measurement of hydrocarbon concentrations is essential to many applications from medical diagnostics to natural gas exploration [1,2,3]. Spectroscopic analyzers strive to use radiation sources in the region of strongest absorption around 3.3  $\mu\text{m}$ . For many years the source of choice has been the optical parametric oscillator [4]. These OPOs feature a wide spectral tuning range and high optical output power. However, their drawbacks are the high investment costs as well as the bulkiness and complexity of use. Also, they tend to have a relatively broad spectral line width compared to other laser technologies. Therefore, a definite need exists for new radiation sources in this wavelength region. Recently, quaternary semiconductor materials opened a new path for simple, compact and easy to use lasers [5]. These newly developed laser diodes have an intrinsic DFB-structure that allows continuous tuning with a spectral line width of approximately 10 MHz (0.3 pm). This diode technology is perfectly suitable for measuring hydrocarbons. The HITRAN Database [6] was used to determine suitable wavelength intervals.

## Laser Characterization

For temperature control the laser is equipped with a Peltier element and a thermoresistant temperature sensor. The highest applicable temperature is 18 °C or 13.73 k $\Omega$ , respectively. The following characterization measurements were conducted by driving the diode in continuous wave mode. The first set of measurements has been carried out to determine the wavelength as a function of current at different temperatures (see Fig. 1). A FTIR spectrometer (Newport 80250 with a DTGS detector) was applied to measure the wavelength.

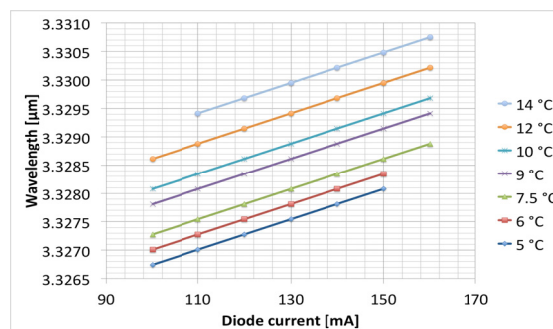


Fig. 1: Wavelength vs. diode current at different temperatures

The second set of measurements was conducted to determine the optical output power as function of current at different temperatures (see Fig. 2). The temperature for these measurements was ranging from 5 °C to 14 °C and the current was varying from 70 mA to 170 mA. The laser threshold was increasing with temperature while the electro-optical efficiency was decreasing. Due to this the curves in Figs.1 and 2 are starting at 100 mA (110 mA at 14 °C).

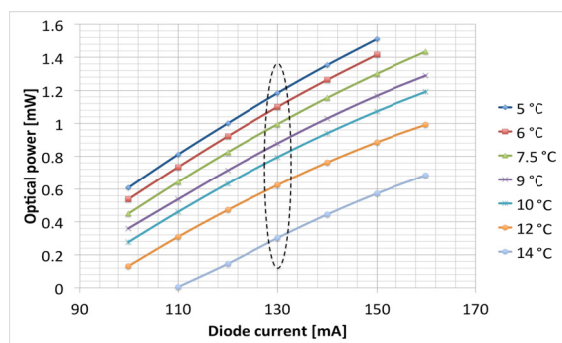


Fig. 2: Optical output power as function of diode current and temperature

### Experimental Setup

The experimental setup is depicted in Fig. 4.

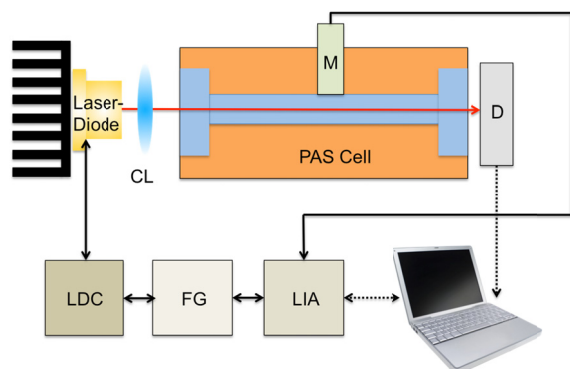


Fig. 4: Schematic setup; CL - collimating lens, LDC - laser diode controller, FG - function generator, LIA - lock-in amplifier, M - microphone, D - power meter

The laser diode is amplitude-modulated with a duty-cycle of 50 % using the square signal from a function generator (FG). Modulation takes place between 70 and 150 mA. The applied frequency is the resonance frequency of the photoacoustic cell (2.75 kHz). A collimating lens (CL) is leading the parallel laser beam centrally through the H-shaped sample cell [4]. An electret microphone (M; Primo EM-158N) detects the photoacoustic signal that is then phase-sensitively amplified by a lock-in amplifier (LIA) that is given reference by the

FG. The power meter (D) allows normalization of the photoacoustic signal according to the optical output power, which is a function of diode current and temperature as shown in Fig. 2. A Labview program is automatically controlling the setup.

### Measurements

The PAS cell was evacuated and subsequently filled with 100 ppm of Methane in Nitrogen (6.0). Calculations of the absorption spectrum proved that the strong absorption lines of methane could be reached best at an operation current of 130 mA. Fig. 4 shows the wavelength as a function of temperature at constant 130 mA, which is corresponding to the circled values in Fig. 2.

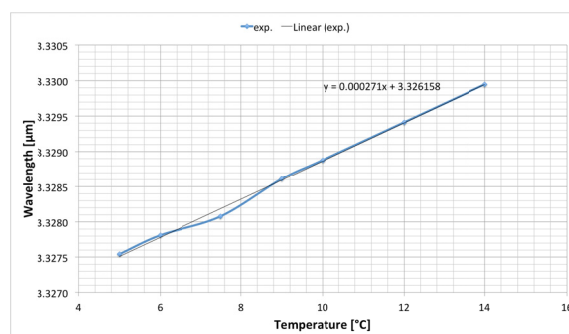


Fig. 4: Wavelength as a function of the diode temperature

Wavelength tuning was achieved by starting at the coldest temperature of 5 °C which was slowly increased. Thus, it was possible to tune the wavelength in 0.02 nm steps. Between each measuring point the system was given a delay time of 5 s to let the laser temperature stabilize.

### Results

With the chosen parameters it was possible to measure sensitively the wavelength interval between 3.3275 and 3.3298 μm. In this region are some characteristic peaks of methane (see Fig.5). The red curve represents the calculated absorption spectrum of methane (at 1013 hPa pressure, 100 ppm in N<sub>2</sub> (6.0) and 20 °C). The experimentally gained photoacoustic signal (blue curve) shows a relatively good agreement with the simulations. The difference at longer wavelength is due to the decreasing optical output power of the laser diode at higher temperatures (see Fig.2). Considering the signal-to-noise ratio the sensitivity is estimated to be in the ppb range.

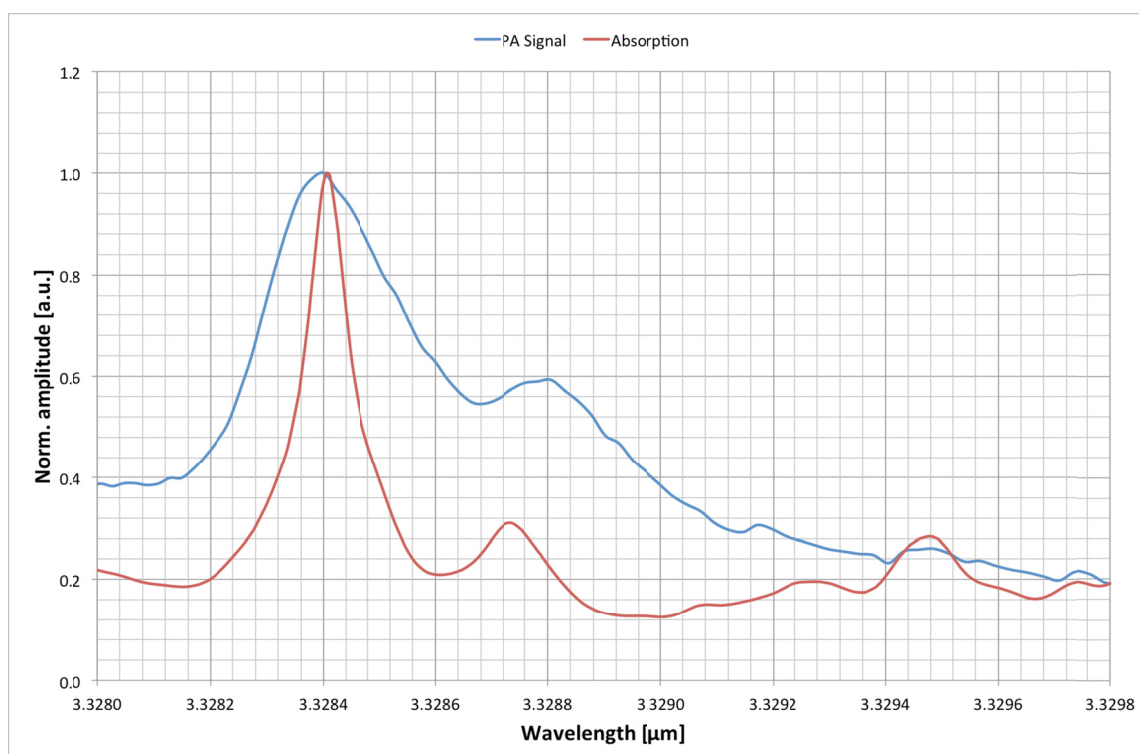


Fig. 5: Photoacoustic signal vs. calculated absorption spectrum; both normalized

## Conclusion

We presented a new optical analyzer for precise methane measurements based on photoacoustic spectroscopy. It uses a newly developed DFB-type semiconductor laser diode emitting around 3.33  $\mu\text{m}$ . We managed to resolve the absorption lines of the two main isotopologues of methane. Due to this an isotope-selective detection seems possible. An optimized modulation with a different duty-cycle, modulation function and modulation depth could further improve our measurements.

## References

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